

## Claims

1. A method for producing a hardened steel part, having cathodic corrosion protection, wherein:
  - a) a coating is applied to a sheet made of a hardenable steel alloy in a continuous coating process, wherein
  - b) the coating is essentially comprised of zinc;
  - c) the coating additionally contains one or more high oxygen affinity elements in a total quantity of 0.1 % by weight to 15 % by weight in relation to the overall coating; and
  - d) the coated steel sheet, at least in some areas, is then brought – with the admission of atmospheric oxygen – to a temperature necessary for the hardening and is heated until it undergoes a microstructural change necessary for the hardening; wherein
  - e) a superficial skin comprised of an oxide of the high oxygen affinity element(s) is formed on the coating; and
  - f) the sheet is formed before or after the heating; and wherein
  - g) the sheet is cooled after sufficient heating, the cooling rate being calculated in order to achieve a hardening of the sheet alloy.
2. The method as recited in claim 1, characterized in that the high oxygen affinity elements used in the mixture are magnesium and/or silicon and/or titanium and/or calcium and/or aluminum and/or manganese and/or boron.

3. The method as recited in claim 1 and/or 2, characterized in that the mixture is applied using the hot dipping process in which a mixture is used that is composed essentially of zinc and the high oxygen affinity element(s).
4. The method as recited in claim 1 and/or 2, characterized in that the coating is applied electrolytically.
5. The method as recited in claim 4, characterized in that in the electrolytic coating, first a zinc layer is deposited and then in a second step, the high oxygen affinity element(s) is/are deposited onto the previously deposited zinc layer.
6. The method as recited in claim 4, characterized in that first, a zinc layer is electrolytically deposited onto the surface of the sheet and then, a coating composed of the high oxygen affinity element(s) is deposited onto the zinc surface.
7. The method as recited in claim 6, characterized in that the high oxygen affinity element(s) is/are vaporized or applied using other suitable methods.
8. The method as recited in claim 1 and/or 2, characterized in that 0.2 wt.% to 5 wt.% of the high oxygen affinity elements is used.
9. The method as recited in one of the preceding claims, characterized in that 0.26 wt.% to 2.5 wt.% of the high oxygen affinity elements is used.
10. The method as recited in one of the preceding claims, characterized in that essentially aluminum is used as the high oxygen affinity element.
11. The method as recited in one of the preceding claims, characterized in that the coating mixture is selected so that during the heating, the coating develops an oxide

skin comprised of oxides of the high oxygen affinity element(s) and the coating is composed of at least two phases, a zinc-rich phase and an iron-rich phase.

12. The method as recited in one of the preceding claims, characterized in that the iron-rich phase has a ratio of zinc to iron of at most 0.95 ( $\text{Zn/Fe} \leq 0.95$ ), preferably from 0.20 to 0.80 ( $\text{Zn/Fe} = 0.20$  to  $0.80$ ), and the zinc-rich phase has a ratio of zinc to iron of at least 2.0 ( $\text{Zn/Fe} \geq 2.0$ ), preferably from 2.3 to 19.0 ( $\text{Zn/Fe} = 2.3$  to  $19.0$ ).
13. The method as recited in one of the preceding claims, characterized in that the iron-rich phase has a ratio of zinc to iron of approx. 30:70 and the zinc-rich phase is comprised of a ratio of zinc to iron of approx. 80:20.
14. The method as recited in one of the preceding claims, characterized in that the coating also has individual areas with zinc contents of  $\geq 90\%$ .
15. The method as recited in one of the preceding claims, characterized in that the coating is embodied so that with an initial thickness of  $15 \mu\text{m}$ , after the hardening process, it develops a cathodic protective action of at least  $4 \text{ J/cm}^2$ .
16. The method as recited in one of the preceding claims, characterized in that the coating with the mixture of zinc and the high oxygen affinity element(s) is produced during the passage through a liquid metal bath at a temperature of between  $425^\circ\text{C}$  and  $690^\circ\text{C}$ , with subsequent cooling of the coated sheet.
17. The method as recited in one of the preceding claims, characterized in that the coating with the mixture of zinc and the high oxygen affinity elements is produced during the passage through a liquid metal bath at a temperature of between  $440^\circ\text{C}$  and  $495^\circ\text{C}$ , with subsequent cooling of the coated sheet.

18. The method as recited in one of the preceding claims, characterized in that the sheet is inductively heated.
19. The method as recited in one of the preceding claims, characterized in that the sheet is inductively heated in the die.
20. The method as recited in one of the preceding claims, characterized in that the sheet is heated in a radiation furnace.
21. The method as recited in one of the preceding claims, characterized in that the cooling takes place in the forming die.
22. The method as recited in one of the preceding claims, characterized in that the cooling is executed during forming by means of cooled forming dies.
23. The method as recited in one of the preceding claims, characterized in that the cooling takes place after the forming in the forming die.
24. The method as recited in one of the preceding claims, characterized in that the cooling takes place in a form hardening die into which the formed sheet is inserted after heating and in which a form-locked engagement occurs between the formed sheet and correspondingly shaped, cooled form hardening dies.
25. The method as recited in one of the preceding claims, characterized in that the heating and cooling takes place in the form hardening die, the heating is executed inductively, and after the inductive heating, the forming die is cooled.
26. The method as recited in one of the preceding claims, characterized in that the forming and the hardening of the part are performed with a roll forming device; the coated sheet, at least in some areas, is heated to the austenitization temperature, roll-

formed before, during, and/or after this, and then cooled in the roll forming die at a cooling rate that results in a hardening of the sheet alloy.

27. A corrosion protection coating for steel sheets that are subjected to a hardening step in which the corrosion protection coating, after being applied to the steel sheet, is subjected to a heat treatment with the admission of oxygen; the coating is essentially comprised of zinc and one or more high oxygen affinity elements in an total quantity of 0.1 wt.% to 15.0 wt.% in relation to the overall mixture; the corrosion protection coating has an oxide skin on the surface, comprised of oxides of the high oxygen affinity element(s) and the coating is composed of at least two phases; and a zinc-rich and iron-rich phase are produced.
28. The corrosion protection coating as recited in claim 27, characterized in that the corrosion protection coating is comprised of high oxygen affinity elements in a mixture of magnesium and/or silicon and/or titanium and/or calcium and/or aluminum and/or boron and/or manganese.
29. The corrosion protection coating as recited in claim 27 and/or 28, characterized in that the corrosion protection coating is a corrosion protection coating applied using a hot dipping process.
30. The corrosion protection coating as recited in claim 29, characterized in that the coating is comprised of a mixture composed essentially of zinc and the mixture also contains one or more high oxygen affinity elements.
31. The corrosion protection coating as recited in claim 27 and/or 28, characterized in that the corrosion protection coating is a corrosion protection coating applied using an electrolytic depositing process.

32. The corrosion protection coating as recited in claim 31, characterized in that the corrosion protection coating is a corrosion protection coating produced through electrolytic depositing of essentially zinc at the same time as one or more high oxygen affinity elements.
33. The corrosion protection coating as recited in claim 31, characterized in that the corrosion protection coating is produced first through electrolytic depositing of essentially zinc and the subsequent vaporization or deposition with other suitable methods of one or more high oxygen affinity elements.
34. The corrosion protection coating as recited in one of the preceding claims, characterized in that the total quantity of the high oxygen affinity elements is from 0.1 to 15.0 wt.% in relation to the overall coating.
35. The corrosion protection coating as recited in one of claims 27 through 33, characterized in that the total quantity of these high oxygen affinity elements is from 0.02 to 0.5 wt.% in relation to the overall coating.
36. The corrosion protection coating as recited in one of claims 27 through 33, characterized in that the total quantity of the high oxygen affinity elements is from 0.6 to 2.5 wt.% in relation to the overall coating.
37. The corrosion protection coating as recited in one of claims 27 through 36, characterized in that essentially aluminum is used as a high oxygen affinity element.
38. The corrosion protection coating as recited in one of claims 27 through 37, characterized in that the iron-rich phase has a ratio of zinc to iron of at most 0.95 ( $\text{Zn/Fe} \leq 0.95$ ), preferably from 0.20 to 0.80 ( $\text{Zn/Fe} = 0.20$  to  $0.80$ ), and the zinc-rich phase has a ratio of zinc to iron of at least 2.0 ( $\text{Zn/Fe} \geq 2.0$ ), preferably from 2.3 to 19.0 ( $\text{Zn/Fe} = 2.3$  to  $19.0$ ).

39. The corrosion protection coating as recited in one of claims 27 through 38, characterized in that the iron-rich phase has a zinc to iron ratio of approx. 30:70 and the zinc-rich phase has a zinc to iron ratio of approx. 80:20.
40. The corrosion protection coating as recited in one of claims 27 through 39, characterized in that the corrosion protection coating also has individual areas with zinc contents of  $\geq 90$  wt.% zinc.
41. The corrosion protection coating as recited in one of claims 27 through 40, characterized in that that with an initial thickness of 15  $\mu\text{m}$ , the corrosion protection coating has a cathodic protection energy of at least 4 J/cm<sup>2</sup>.
42. A hardened steel part manufactured using a method as recited in one of claims 1 through 27, with a corrosion protection coating as recited in one of claims 27 through 41.
43. The hardened steel part as recited in claim 42, characterized in that the part is comprised of a hot rolled or cold rolled steel band with a thickness of  $\geq 0.15$  mm and with a concentration range of at least one of the alloy elements within the following weight percentage limits:

carbon	up to 0.4,	preferably 0.15 to 0.3
silicon	up to 1.9,	preferably 0.11 to 1.5
manganese	up to 3.0,	preferably 0.8 to 2.5
chromium	up to 1.5,	preferably 0.1 to 0.9
molybdenum	up to 0.9,	preferably 0.1 to 0.5
nickel	up to 0.9,	
titanium	up to 0.2,	preferably 0.02 to 0.1
vanadium	up to 0.2	

tungsten	up to 0.2,	
aluminum	up to 0.2,	preferably 0.02 to 0.07
boron	up to 0.01,	preferably 0.0005 to 0.005
sulfur	max. 0.01,	preferably max. 0.008
phosphorus	max 0.025,	preferably max. 0.01
residual iron and impurities.		



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This object is attained by means of a corrosion protection with the defining characteristics of claim 27. The claims dependent thereon disclose advantageous modifications of this.

In the method according to the present invention, a hardenable steel sheet is provided with a coating comprised of a mixture of mainly zinc and one or more high oxygen affinity elements such as magnesium, silicon, titanium, calcium, aluminum, boron, and manganese, containing 0.1 to 15% by weight of the high oxygen affinity element, and the coated steel sheet, at least in some areas, is heated to a temperature above the austenitization temperature of the sheet alloy with the admission of oxygen, and is formed before or after this; after sufficient heating, the sheet is cooled, the cooling rate being calculated to produce a hardening of the sheet alloy. The result is a hardened part made of a sheet steel that provides a favorable level of cathodic corrosion protection.

The corrosion protection for steel sheets according to the present invention, which first undergo a heat treatment and are then formed and hardened, is a cathodic corrosion protection that is essentially zinc-based. According to the invention, the zinc that comprises the coating is mixed with 0.1% to 15% of one or more high oxygen affinity elements such as magnesium, silicon, titanium, calcium, aluminum, boron, and manganese, or any mixture or alloy thereof. It has turned out that such small quantities of a high oxygen affinity element such as magnesium, silicon, titanium, calcium, aluminum, boron, and manganese achieve a surprising effect in this specific use.

- Fig. 23     qualitatively depicts the phase formation as a “leopard pattern” in coatings according to the invention;
- Fig. 24     is a flowchart depicting the possible process sequences according to the invention;
- Fig. 25     is a graph depicting the distribution of the elements aluminum, zinc, and iron depending on the depth of the surface coating before the sheet is annealed; and
- Fig. 26     is a graph depicting the distribution of the elements aluminum, zinc, and iron depending on the depth of the surface coating after the sheet is annealed, as proof of the formation of a protective aluminum oxide skin on the surface.

Approximately 1 mm thick steel sheets with a corrosion protection coating that is the same on both sides, with a layer thickness of 15  $\mu\text{m}$  were manufactured and tested. The sheets were placed for 4 minutes 30 seconds in a 900°C radiation furnace and then rapidly cooled between steel plates. The time between removal of the sheets from the furnace and the cooling between the steel plates was 5 seconds. The heating curve of the sheets during the annealing in the radiation furnace essentially followed the curve shown in Fig. 1.

Then, the test specimens obtained were analyzed for visual and electrochemical differences. Assessment criteria here included the appearance of the annealed steel sheets and the protection energy. The protection energy is the measure for the electrochemical protection of the coating, determined by means of galvanostatic dissolution.

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of approx.  $-0.6$  V sets in. This potential also lies significantly below the steel potential. After a measurement time of approx. 3,500 seconds, this part of the coating is depleted and the required potential for dissolution of the coating approaches the steel potential. After the annealing, this coating consequently provides a cathodic corrosion protection in addition to the barrier protection. Up to a measurement time of 3,500 seconds, the potential has a value of  $\leq -0.6$  V so that an appreciable cathodic protection is maintained over a long time period, even if the sheet has been brought to austenitization temperature. Fig. 7 shows the potential/time graph.

#### Example 4 (according to the invention)

The sheet is conveyed through a heat melting bath or zinc bath with a zinc content of 99.8% and an aluminum content of 0.2%. During the annealing, aluminum contained in the zinc coating reacts to atmospheric oxygen and forms a protective  $\text{Al}_2\text{O}_3$  skin. Continuous diffusion of the high oxygen affinity aluminum to the surface causes this protective skin to form and keeps it maintained. After annealing, the sheet has a silver-gray surface without defects. During annealing, diffusion transforms the zinc coating that was originally approx.  $15\text{ }\mu\text{m}$  thick into a coating approx. 20 to  $25\text{ }\mu\text{m}$  thick; this coating (Fig. 8) is composed of a dark-looking phase with a Zn/Fe composition of approx. 30/70 and a light region with a Zn/Fe composition of approx. 80/20. The surface of the coating has been verified to have an increased aluminum content. The detection of oxides on the surface indicates the presence of a thin protective coating of  $\text{Al}_2\text{O}_3$ .

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below that 15  $\mu\text{m}$ -thick coatings and the above-described processing and testing conditions yield a cathodic corrosion protection energy of at least 4  $\text{J}/\text{cm}^2$ .

A zinc coating that has been electrolytically deposited onto the surface of the steel sheet cannot by itself provide a corrosion protection according to the invention, even after a heating step that brings it to a temperature higher than the austenitization temperature. However, the present invention can also be achieved with an electrolytically deposited coating according to the invention. To accomplish this, the zinc, together with the high oxygen affinity element(s) can be simultaneously deposited in an electrolysis step onto the surface of the sheet so that the surface of the sheet is provided with a coating of a homogeneous structure that contains both zinc and the high oxygen affinity element(s). When heated to the austenitization temperature, a coating of this kind behaves in the same manner as a coating of the same composition that is deposited on the surface of the sheet by means of hot-dip galvanization.

In another advantageous embodiment form, only zinc is deposited onto the surface of the sheet in a first electrolysis step and the high oxygen affinity element(s) is/are deposited onto the zinc layer in a second electrolysis step. The second layer comprised of the high oxygen affinity elements here can be significantly thinner than the zinc layer. When such a coating according to the invention is heated, the outer covering – which is composed of the high oxygen affinity element(s) and is situated on the zinc layer – oxidizes, thus protecting the underlying zinc with an oxide skin. Naturally, the high oxygen affinity element(s) is/are selected so that they do not vaporize from the zinc layer or do not oxidize without leaving behind a protective oxide skin.

Translation Key for Figs.

Fig. 1:

Temperatur – temperature

Zeit – time

Ofentemperatur – furnace temperature

Blechtemperatur – sheet temperature

Figs. 2, 4, 6, 8, 11, 13, 17: metallographic analysis and surface analysis

Figs. 3, 5, 7, 9, 12, 14, 16, 18, 19:

Stahlpotential – steel potential

Messzeit – measurement time

Fig. 20:

Stahlpotential – steel potential

Messzeit – measurement time

[shaded area indicated:] Area used to evaluate corrosion protection

Fig. 21 (top to bottom):

protection energy

example

Fig. 22 (left to right):

protection energy

annealing in radiation furnace

rapid heating

Figs. 25 & 26:

percentages by weight of the elements Fe, Al, and Zn

average sputtering depth /  $\mu\text{m}$

Fig. 24:

